



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C04B 35/00, A61L 27/00</b> <b>A61K 6/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 90/11979</b> <b>(43) International Publication Date:</b> 18 October 1990 (18.10.90)
<b>(21) International Application Number:</b> PCT/SE90/00207 <b>(22) International Filing Date:</b> 30 March 1990 (30.03.90)  <b>(30) Priority data:</b> 8901294-2                      10 April 1989 (10.04.89)                      SE  <b>(71) Applicant (for all designated States except US):</b> STIFTELSEN CENTRUM FÖR DENTALTEKNIK OCH BIOMATERIAL I HUDDINGE [SE/SE]; Institutionsväg- en 6, Plan 7, S-141 04 Huddinge (SE).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> HERMANSSON, Leif [SE/SE]; Brunnsgården, S-740 20 Brunna (SE). FORBERG, Sevald [SE/SE]; Bastuhagsvägen 35, S-122 42 Enskede (SE). JIANGOU, Li [CN/SE]; Wenner-Gren Center, Sveavägen 166, S-113 46 Stockholm (SE).		<b>(74) Agent:</b> HYNELL, Magnus; Hynell Patenttjänst AB, Box 236, S-683 02 Hagfors (SE).  <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), + CH, CH (European patent), CM (OAPI patent), DE, + DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Swedish).</i>
<b>(54) Title:</b> COMPOSITE CERAMIC MATERIAL AND METHOD TO MANUFACTURE THE MATERIAL  <b>(57) Abstract</b> <p>The present invention relates to a method to manufacture a composite ceramic material having a high strength combined with bioactive properties, when the material is used as a dental or orthopedic implant, which includes preparing a powder mixture, mainly comprising partly a first powder, which in its used chemical state will constitute a bioinert matrix in the finished material, and partly a second powder, mainly comprising a calcium phosphate-based material. The invention is characterized in that said first powder comprises at least one of the oxides belonging to the group consisting of titanium dioxide (TiO<sub>2</sub>), zirconium oxide (ZrO<sub>2</sub>) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), in that said second powder mainly comprises at least one of the compounds hydroxylapatite and tricalcium phosphate, in that a raw compact is made of said powder mixture and in that said raw compact is densified through an isostatic pressing in a hot condition (HIP) at a pressure higher than 50 MPa, a composite material being obtained, in which said matrix comprises one or several metal oxides of said first powder, in which matrix said compound hydroxylapatite and/or tricalcium phosphate is evenly dispersed. The invention also relates to a composite ceramic material as well as a body, completely or partially made of this material.</p>		

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COMPOSITE CERAMIC MATERIAL AND METHOD TO MANUFACTURE THE MATERIAL  
TECHNICAL FIELD

The present invention relates to a composite ceramic material having a high strength combined with bioactive properties when the material is used as a dental or orthopedic  
5 implant. The invention relates also to a method to manufacture the composite ceramic material.

BACKGROUND ART

Ceramic materials and particularly structural ceramic materials generally have a high resistance to corrosion and erosion. This is true of e.g. several oxides, nitrides, carbides and borides. Also, said materials have no toxic properties. When used as implant materials said materials are completely inactive, i.e. neither positive nor negative reactions  
10 with surrounding tissues take place, and consequently it is possible to attain a biological integration to bone tissue without any intermediate connective tissue. Such materials are termed inert when used as implant materials. These properties make several oxides, nitrides, carbides and borides  
15 potentially very valuable as inert dental and orthopedic implant materials.

However, it is desirable that materials having a favorable biocompatibility are not only inert, i.e. able to fasten  
25 mechanically to a bone tissue, but also bioactive, i.e. the implant can be bonded chemically to a bone tissue. Oxides, nitrides, carbides and borides do not have this property. On the other hand it is known that phosphate-based materials, having a chemical composition similar to the "inorganic" or "ceramic" matter in bone tissue, can display bioactive properties. Such a phosphate-based material is e.g.  
30 hydroxylapatite,  $\text{Ca}(\text{PO}_4)_3$ , However, a synthetic hydroxylapatite has a low tensile toughness and hence a low strength and also a tendency to gradually develop a continuous crack  
35 growth. Another example of a bioactive material having a calcium phosphate-base is tricalcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$ , but this compound has an unsatisfactory strength. Also, it

has a not negligible water solubility and consequently may be dissolved before the bond to the bone tissue has developed. Thus, in this respect, hydroxylapatite is preferred as compared to tricalcium phosphate.

5

#### DISCLOSURE OF THE INVENTION

The object of the invention is to suggest a composite ceramic material having a so called duo-quality, i.e. a high strength combined with a bioactivity. This and other objects  
10 can be attained by using a material, which comprises, when it is used as an implant material, an inert matrix having a high strength and in the matrix evenly distributed 5-35 percent by volume of at least one second phase, which mainly comprises at least one material having a calcium phosphate-  
15 base. This calcium phosphate-base can e.g. be hydroxylapatite and/or tricalcium phosphate, while the matrix can comprise mainly one or several oxides and/or nitrides. The matrix comprises preferably mainly one or several oxides belonging to the group which comprises titanium dioxide,  
20 zirconium oxide and aluminum oxide.

The used hydroxylapatite can be entirely synthetic or consist of a bone ash, which also contains other compounds than hydroxylapatite in small contents.

25

The material is produced by preparing a powder mixture, which mainly consists of partly a first powder, which in the condition the powder material is in during the admixture or it will obtain after a subsequent chemical reaction  
30 can form a biologically inert matrix in the finished material when it is to be used as an implant material, and partly a second powder, mainly consisting of a material having a calcium phosphate-base. A raw compact is made of this powder mixture and densified.

35

According to one aspect of the invention said raw compact is densified by a hot isostatic pressing at a pressure of

higher than 50 MPa, preferably at a pressure of at least 150 MPa and preferably not more than 250 MPa. The raw compact is in this case suitably produced by a cold isostatic compacting, which precedes the hot isostatic compacting, which is facilitated by the admixture of the calcium phosphate powder into the oxide powder. The hot isostatic compacting preferably is carried out at a temperature of 900-1300°C. Despite the comparatively low temperature during the hot isostatic compacting it is possible to attain a density of at least 97 %, if the matrix consists of oxides. The comparatively low sintering temperature is advantageous, e.g. for the following reasons:

- The grain growth is limited, which favors a high strength;
- A decomposition of the calcium phosphate material (hydroxylapatite or the like) is avoided or limited to an acceptable extent; and
- Undesirable reactions between oxides, e.g. titanium dioxide, and the calcium phosphates are prevented.

When the powder material is consolidated, no chemical reactions take place. The powder mixture suitably is composed in such a manner, that the calcium phosphate-phase will appear as small islands, i.e. as discrete particles, in the matrix, which according to the first preferred embodiment of the invention consists of one or several oxides belonging to the group, which comprises titanium dioxide, zirconium oxide and aluminum oxide. One might expect that 5-35 percent by volume of calcium phosphate material in the inert matrix is not sufficient to ensure the desired bioactivity but at the same time will result in a risk of a substantial deterioration of the strength properties. However, we have found that these fears are groundless. Thus, clinical experiments, performed on living animals, have shown, that the material according to the invention has a bioactivity, which is entirely comparable to the bioactivity of pure hydroxylapatite. Thus, it is not necessary to coat the inert matrix with pure hydroxylapatite in order to ob-

tain the desirable bioactivity, which otherwise is customary according to known practice. However, the admixture of calcium phosphate material into the matrix probably must be very finely dispersed and even in order to obtain a very large number of islands per exposed surface unit, the distance between adjacent islands of calcium phosphate at the same time being very small. These conditions probably will facilitate the addition of a new bone tissue, but the causal relations have not been completely explained. The very finely dispersed and even nature of the distribution of the calcium phosphate fraction in the matrix can also explain the retained very high strength. Thus, provided one regard the calcium phosphate particles as defects of the matrix, it is possible to calculate the largest possible size of the calcium phosphate islands in different oxide materials in order to obtain a certain so called critical intensity factor (critical toughness), known for the matrix. Thus, if the matrix is tougher, the islands can be larger than in a brittle matrix and vice versa. These theoretical considerations and practical results lead to the following recommendations for a composite consolidated material consisting of a matrix, which comprises metal oxides, and a calcium phosphate material dispersed in the matrix, preferably hydroxylapatite.

25	Matrix	Maximum size of the calcium phosphate particles	Mean distance between the calcium phosphate particles
	TiO <sub>2</sub>	10 $\mu$ m	Max. 5 $\mu$ m, pref. max. 2 $\mu$ m
30	Al <sub>2</sub> O <sub>3</sub>	15 $\mu$ m	"
	ZrO <sub>2</sub>	30 $\mu$ m	"

Thus, as regards the strength, zirconium oxide is preferred to aluminum oxide, which in its turn is better than titanium oxide. Also, the oxides differ as to their chemical resistance. Thus, whereas the temperature during the hot isostatic pressing should not be higher than 1000°C, when the

matrix is composed of titanium dioxide, it can be as high as 1300°C and preferably 1100-1250°C, when a matrix of aluminum oxide and/or zirconium oxide is used.

5 Whereas according to known practice one believes that it is necessary to provide an implant with a coat, which entirely consists of a bioactive material, which means that in certain cases the implant has been provided with an outer coat of a calcium phosphate material, according to the present  
10 invention it is possible to use the duo-properties of the composite material according to the invention, an extra outer coat of hydroxylapatite or the like then not being necessary. However, it is also, within the scope of the present invention, possible per se to cover a "duo-material",  
15 completely or partially, with layers of materials having another composition or to produce implants, in which different parts have different compositions, including at least one part consisting of a composite material according to the invention having duo-properties and at least one part  
20 consisting of a homogenous material, e.g. a ceramic material without any admixture of a calcium phosphate material or an entirely metallic material. These and other aspects of the invention are also set forth in the patent claims and will be further elucidated in the following description of a  
25 few preferred embodiments.

According to an alternative process of producing a composite material according to the invention a powder mixture is prepared, in which the first powder mainly consists of  
30 elementary silicon, whereas the second powder in this case mainly is tricalcium phosphate having a particle size of not more than 5  $\mu\text{m}$ . A raw compact is made from the powder, composed of 5-15 percent by volume tricalcium phosphate and the remainder silicon (and pores), and nitridized by means  
35 of nitrogen gas. As an alternative principally also ammonia and other nitridization agents can be used. Through the nitridization the silicon is combined with nitrogen to form

silicon nitride  $\text{Si}_3\text{N}_4$  and due to the mass build-up the raw compact is condensed to a density of between 65 and 85 % of the theoretical maximum density. Thus, this composite ceramic material is considerably more porous than that material, which is densified through a hot isotatic pressing, e.g. according to the embodiment described above, which of course unfavorably influences the strength. However, this can to a high degree be made up for due to the fact that silicon nitride is a very strong material. As far as the bioactivity is concerned, the porosity has the valuable effect, that in the pores minor surface-located areas of tricalcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  are exposed. Thus, when a bone growth inwards into the matrix, i.e. into the pore system of the silicon nitride, takes place, Ca-ions as well as phosphate groups are available, which are the necessary building units for a bone growth.

#### BRIEF DESCRIPTION OF DRAWINGS

The invention will now be explained in more detail by means of a few illustrative examples and experiments carried out, reference being made to the accompanying drawings, in which: Fig. 1 shows a microstructure of a material according to a first preferred embodiment according to the invention; Fig. 2 is a drawn picture, based on an X-ray photograph, which shows how an implant according to the invention has adhered to a natural bone material; Fig. 3 shows a longitudinal section of a product according to a possible embodiment of the invention; Fig. 4 shows a longitudinal section of a product according to another possible embodiment of the invention; and Fig. 5 shows a longitudinal section of a product according to an additional possible embodiment of the invention.

#### DESCRIPTION OF EXPERIMENTS CARRIED OUT AND EMBODIMENTS

Raw materials used in the trials are listed in Table 1. Monolithic materials (titanium dioxide and hydroxylapatite respectively) as well as composite materials (combinations



of oxides and calcium phosphate materials), Table 2, were produced from powders of these raw materials. The powder mixtures and a silicon nitride grinding agent in petroleum ether were admixed in a ball mill and were ground for 20 h. Subsequent to an evaporation in an evaporator raw compacts were produced from the powder mixtures by a cold isostatic compacting (CIP) at a pressure of 300 MPa. The raw compacts thus obtained were encased in glass and densified by a hot isostatic pressing (HIP) at a pressure of 200 MPa for 1 h at a maximum temperature of 925°C for the TiO<sub>2</sub>-based materials and at 1225°C for the other materials. Subsequent to the densification the materials displayed a density of more than 99 % of the theoretical maximum density. The HIP-temperatures and the obtained densities are also shown in Table 2.

Table 1 - Raw materials

Designation	Description
BA	Hydroxylapatite of bone ash
HA	Hydroxylapatite, grade Merck
20 TCP	β -tricalcium phosphate, grade Merck
A	α -aluminum oxide, AKP-30, Sumitomo
R	Titanium dioxide, Tioxide Ltd
Z	Zirconium dioxide (including 3 mol-% Y <sub>2</sub> O <sub>3</sub> )

Table 2 - Powder mixtures which have been compacted by a hot isostatic pressing; densities of HIP-produced specimens

Specimen No.	Powder, % by volume	HIP-temp. °C	Density g/cm <sup>3</sup>	
			Recorded	Theoretical
1	70HA/30A	1225	3.39	3.40
2	25HA/75A	1225	3.75	3.77
3	15BA/85A	1225	3.85	3.85
4	15HA/85R	925	4.02	4.09
35 5	7.5TCP/7.5HA/85A	1225	3.77	3.85
6	7.5TCP/7.5HA/85R	925	4.04	4.09
7	15HA/85Z	1225	5.64	5.65

Table 3

	Specimen no.	Tensile strength (MPa)	Weibull- module (m)	Toughness (MPam <sup>1/2</sup> )	Hardness (5N) (GPa)
5	HA	110	18	1.1 <u>±</u> 0.1	3.9 <u>±</u> 0.3
	1	250	n.d.*	2.0	7.1
	2	535	n.d.*	4.0	20.2
	3	601	19	3.5	18.9
	4	252	9	2.9	8.4
10	5	446	10	3.4	17.8
	6	397	n.d.*	2.6	10.9
	7	820	n.d.*	>7	13
	A	400-560	-	4	22
	R	405	10	-	12
15	Z	980	n.d.*	>7	14
	* not measured				

\* not measured

Test bars were made with the size 3x3x30 mm. The test bars were examined in a three-point test to measure the compressive strength in bending. The Weibull-modules were measured. The toughness was measured using Vicker's indentation depth-method, as well as the hardness at a load of 10 N och 5N respectively. Some specimens were etched for 20 seconds in a 0.1 % HF-solution in order to study the microstructure in SEM.

In order to study the bioactive properties of the materials cylinders were made with a diameter of 3.1 mm and a length of 7 mm. Identical specimens of pure aluminum oxide (negative control) and pure hydroxylapatite (positive control) were also made to be used as reference materials. The implants were inserted by operation in a large hole (3.2 mm diameter) in lateral cortex in rabbits (femora-rabbit från New Zeeland). After a healing period of three months the animals were put to death and the implants were examined by X-ray radiography, subsequent to the removal of surrounding soft tissue.

Fig. 1 shows the microstructure of a material according to

the invention, being composed of 15 percent by volume hydroxylapatite, the remainder being aluminum oxide (specimen 3). The hydroxylapatite-phase is evenly distributed throughout the aluminum oxide-matrix, in which the hydroxylapatite forms particles (grains) or islands (insulets) having a maximum length of  $< 6 \mu\text{m}$ . The specimen is somewhat overetched in Fig. 1 in order to be able to identify the microstructure more easily. Some of the smallest grains can be pores. An X-ray diffraction analysis showed that no phase alterations had taken place during the HIP-treatment.

The mechanical properties are shown in Table 3. As is expected, the aluminum oxide-based duo-ceramic materials, specimens 1, 2, 3 and 5, are stronger than the titanium dioxide-based materials, specimens 4 and 6. The strength level of the aluminum oxide-based duo-ceramic materials is comparable to the strength level of commercial dental implants made of polycrystalline aluminum oxide, which is 400-560 MPa. The tensile strength is also comparable. The zirconium oxide-based duo-ceramic materials have the highest strength and tensile strength. The results show, that the duo-ceramic materials according to the present invention can be used for dental implants, at least as regards the mechanical properties. This is particularly true of those duo-ceramic materials according to the invention, which are based on aluminum oxide and zirconium oxide, but also the titanium-based duo-ceramic materials in all likelihood can be used as implants, at least in those instances when the mechanical properties are a critical factor.

Fig. 2 shows in a drawing, based on an X-ray radiograph a ceramic cylinder, made of specimen no. 3 in Table 3 and inserted by operation. A new cortical bone material has grown towards the implant (at a) as well as along the surface of the implant (at b). The pattern of bone growth for the duo-ceramic material according to the invention is mainly identical with that for pure hydroxylapatite, as was shown in

a comparison test. A similar pattern was also obtained with specimens no.4 and no. 7, which had a matrix of titanium dioxide and zirconium oxide respectively.

5        These trials show, that bioactive ceramic materials having  
a high strength can be produced by means of a hot isostatic  
pressing of a raw compact, which is composed of at least  
two powder fractions, a bioactive phase being obtained, which  
10       consists of hydroxylapatite and is evenly distributed in an  
oxidic matrix, which gives the material the required strength.  
The bioactive phase appears as distinct points, the size of  
which can be allowed to vary depending on the strength of  
the matrix, but the mean distance between adjacent points  
must be smaller than 5  $\mu\text{m}$ , preferably smaller than 2  $\mu\text{m}$ .

15       In the description above for the invention it has been men-  
tioned that it, within the scope of the inventive concept,  
also is possible to produce compacts (bodies), in which dif-  
ferent parts have different compositions. This will now be  
20       illustrated by means of a few possible examples. According  
to a first embodiment of this aspect of the invention 15  
percent by volume hydroxylapatite powder and 85 percent by  
volume zirconium oxide powder are mixed. The powder is pre-  
pared in the same manner as is explained in the description  
25       above of experiments carried out. The powder mixture is  
poured into a polymer can to fill the can up to half its  
height. Pure aluminum oxide without any admixture of any  
substance is then added to fill the can completely. The can  
is closed and the powder is isostatically compressed in a  
30       cold condition at 300 MPa. The compact specimen is then iso-  
statically compressed in a hot condition at 1225° for 1 h and  
at a pressure of 160 MPa. The compact specimen is cut into  
test bars, in which the center line roughly corresponds to  
the boundary between pure aluminum oxide and the aluminum  
35       oxide/hydroxylapatite-mixture. The test bars (7 of them)  
with the dimensions 35x3x3 mm are examined using a three-  
point-bend-testing method. A mean value of the tensile  
strength was measured to 720 MPa (the lowest value was 540

MPa and the highest 810 MPa).

5 It is also possible to produce a material similar to the previous one by producing two separate raw compacts, one of them consisting of a powder mixture of a calcium phosphate powder and an oxidic powder and the other one solely consisting of an oxidic powder, and combining the raw compacts through a common isostatic compacting in a hot condition. Fig. 3 shows schematically an example of a work piece  
10 produced in this way, in which the joint-ball can consist of a ceramic substance made of pure oxide and the stem can consist of a duo-ceramic substance according to the invention.

15 Fig. 4 shows schematically another example. In this instance a pure oxidic powder 1 is coated with a duo-ceramic powder 2, powder 2 being partially covering powder 1, subsequent to which the combined powder is isostatically compressed in a cold condition and after that is encased and isostatically  
20 compressed in a hot condition.

Fig. 5 shows the opposite instance, namely that a raw compact 3 of a duo-ceramic powder according to the invention partially is coated with an oxidic powder 4, before the compact is consolidated through a combined isostatic pressing  
25 in a cold condition followed by an isostatic pressing in a hot condition.

30 A compact of a duo-ceramic material according to the invention can also be treated in order to remove the bioactive phase in the surface area of a section of the component. This can be done through a chemical dissolving of the calcium phosphate phase in the surface layer or through blasting. In either case small cavities are obtained in those  
35 areas where the phosphate material previously was present and these cavities can function as liquid reservoirs, in case implants for joints are to be produced. Thus, a cer-

12

tain amount of liquid can be kept and in this way the friction can be reduced within those areas, where a sliding is to take place in the joint. Of course, the remaining parts of the duo-ceramic work-piece are to be left intact in order to be able to utilize the bioactive properties of the duo-ceramic work-piece, where this property is desirable.

10

## CLAIMS

1. Method to manufacture a composite ceramic material having a high strength combined with bioactive properties, when the material is used as a dental or orthopedic implant, which comprises preparing a powder mixture, mainly consisting partly of a first powder, which as to its chemical state is designed to constitute a bioinert matrix in the finished material, and partly of a second powder mainly consisting of a calcium phosphate-based material, c h a r a c t e r i z e d in that the first powder comprises at least one oxide belonging to the group consisting of titanium dioxide ( $\text{TiO}_2$ ), zirconium oxide ( $\text{ZrO}_2$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ), in that the second powder mainly comprises at least one of hydroxylapatite and tricalcium phosphate, in that a raw compact is made of the powder mixture and in that said raw compact is densified through a isostatic pressing in a hot condition (HIP) at a pressure higher than 50 MPa, a composite material being obtained, in which the matrix comprises one or several metal oxides of said first powder, in which matrix said hydroxylapatite and/or tricalcium phosphate are evenly dispersed.
2. Method according to claim 1, c h a r a c t e r i z e d in that said raw compact is densified at a pressure of at least 150 MPa and not more than 250 MPa and at a temperature of 900-1300°C.
3. Method according to claim 2, c h a r a c t e r i z e d in that said first powder mainly comprises titanium dioxide and in that said raw compact is densified through an isostatic pressing in a hot condition at a temperature of 900-1000°C.
4. Method according to claim 2, c h a r a c t e r i z e d in that said first powder mainly comprises aluminum oxide and/or zirconium oxide and in that said raw compact is densified

through an isostatic pressing in a hot condition at a temperature of 1100-1250°C.

- 5      5. Method according to any of claims 1-4, c h a r a c -  
t e r i z e d in that said second powder comprises hydrox-  
ylapatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ .
- 10      6. Method according to claim 2, c h a r a c t e r i z e d  
in that said raw compact is densified to at least 97 % of  
the theoretical maximum density, i.e. its full density.
- 15      7. Method according to any of claims 1-6, c h a r a c -  
t e r i z e d in that said powder mixture is composed in  
such a way, that said matrix will comprise 5-35, preferably  
10-25 percent by volume of said hydroxylapatite and/or  
tricalcium phosphate.
- 20      8. Modification of the method according to claim 1, c h a -  
r a c t e r i z e d in that a raw compact is prepared of  
the powder mixture, in that said first powder mainly comp-  
rises silicon, in that said second powder mainly comprises  
hydroxylapatite and/or tricalcium phosphate, preferably  
mainly tricalcium phosphate, and in that the raw compact,  
25      prepared of said powder mixture, is nitridized, said sili-  
con being combined with nitrogen in order to form silicon  
nitride and the raw compact being densified due to mass  
growth.
- 30      9. Method according to claim 8, c h a r a c t e r i z e d  
in that said raw compact is densified, due to mass growth,  
to a density of 65-85 % of the theoretical maximum density.
- 35      10. Composite ceramic material having a high strength com-  
bined with bioactive properties, when the material is used  
as a dental or orthopedic implant, consisting of, when it  
is used as an implant, an inert matrix having a high strength  
and a second phase, evenly dispersed in the matrix and main-



ly comprising at least one calcium phosphate-based material, characterized in that said calcium phosphate base is included in an amount of 5-35, preferably 10-25 percent by volume in said matrix and in that it is present in the matrix as particles having a maximum size of 30  $\mu\text{m}$ , the maximum mean distance between the particles being 5  $\mu\text{m}$ , preferably 2  $\mu\text{m}$ .

11. Material according to claim 10, characterized in that said matrix mainly comprises zirconium oxide and in that the maximum size of the calcium phosphate particles is 30  $\mu\text{m}$ .

12. Material according to claim 10, characterized in that said matrix mainly comprises aluminum oxide and in that the maximum size of the calcium phosphate particles is 15  $\mu\text{m}$ .

13. Material according to claim 10, characterized in that said matrix mainly comprises titanium dioxide and in that the maximum size of the calcium phosphate particles is 10  $\mu\text{m}$ .

14. Material according to claim 10, characterized in that said matrix mainly comprises silicon nitride.

15. Material according to claim 14, characterized in that said calcium phosphate material comprises tricalcium phosphate, which amounts to 5-15 percent by volume of the material.

16. Material according to any of claims 10-13, characterized in that its density is at least 97 % of the theoretical maximum value.

16

17. Material according to claim 14 or 15, characterized in that its density is 65-85 % of the theoretical maximum value and in that it has a pore system, in which calcium phosphate is exposed in the pores.

5

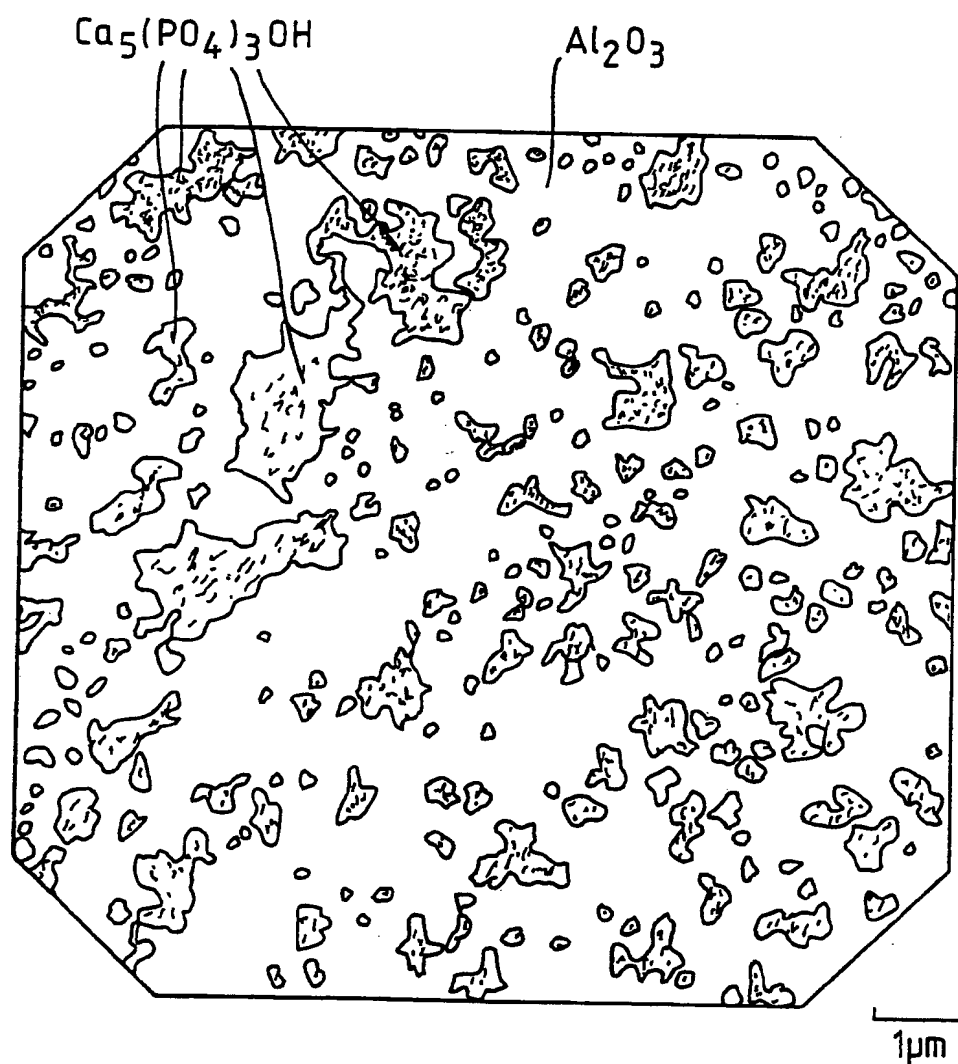
18. Body only partially made of a material according to any of claims 10-13, which material forms one or several parts of said body, characterized in that one or several other parts of said body mainly are made of one or several of the oxides titanium dioxide ( $\text{TiO}_2$ ), zirconium oxide ( $\text{ZrO}_2$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ).

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1/2

Fig. 1.



SUBSTITUTE SHEET

Fig. 2.

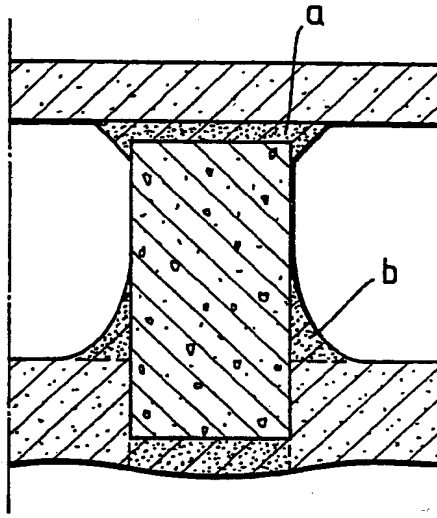


Fig. 3.

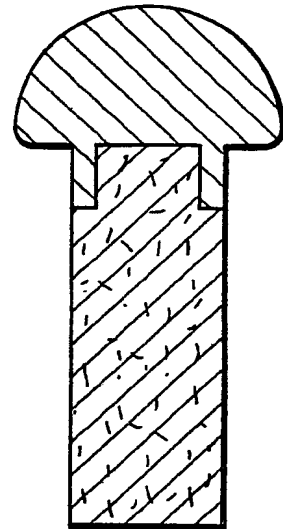


Fig. 4.

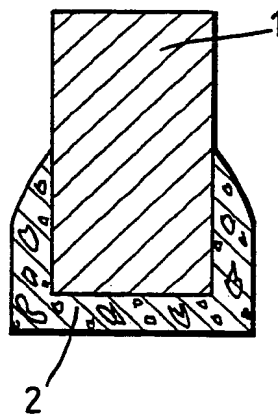
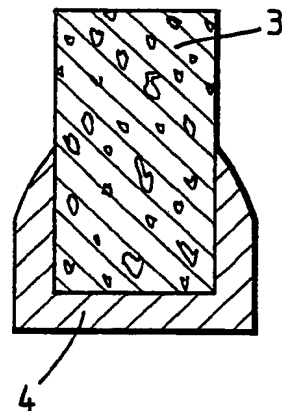


Fig. 5.



# INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 90/00207

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <b>IPC5: C 04 B 35/00, A 61 L 27/00, A 61 K 6/06</b>						
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black; text-align: left;">Classification System</th> <th style="width: 75%; border: 1px solid black; text-align: left;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">IPC5</td> <td style="border: 1px solid black; padding: 5px;">A 61 C; A 61 K; A 61 L; C 04 B</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	A 61 C; A 61 K; A 61 L; C 04 B
Classification System	Classification Symbols					
IPC5	A 61 C; A 61 K; A 61 L; C 04 B					
SE,DK,FI,NO classes as above						
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>						
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>				
X	Chemical Abstracts, volume 108, no. 2, 11 January 1988, (Columbus, Ohio, US), see page 336, abstract 11277v, & JP,, 62142565 (TAMATOSHI NOBUYUKI) 1987 --	1,5,7, 10,11				
X	DE, A1, 3301122 (OSBORN, JOHANNES-FRIEDRICH, DR.) 19 July 1984, see page 5, line 8 - line 10 --	1,3,5-7, 10,13				
A	DE, A1, 2928007 (RIESS, GUIDO DR.) 15 January 1981, see the whole document -- -----	1-18				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:<sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>						
<b>IV. CERTIFICATION</b>						
Date of the Actual Completion of the International Search <b>2nd July 1990</b>		Date of Mailing of this International Search Report <b>1990 -07- 10</b>				
International Searching Authority <div style="text-align: center;"><b>SWEDISH PATENT OFFICE</b></div>		Signature of Authorized Officer <div style="text-align: center;">May Hallne <i>May Hallne</i></div>				

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 90/00207**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on **90-05-07**.  
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A1- 3301122	84-07-19	EP-A-B- 0116298	84-08-22
DE-A1- 2928007	81-01-15	CA-A- 1153505	83-09-13
		EP-A- 0023608	81-02-11
		JP-A- 56018864	81-02-23
		US-A- 4599085	86-07-08